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REACTION OF ESTERS OF N-BUTYL-N-ISOBUTENYLAMIDO- AND BIS(N-BUTYL-N-ISOBUTENYLAMIDO)PHOSPHORUS ACIDS WITH OXYGEN AND HALOGEN-CONTAINING COMPOUNDS

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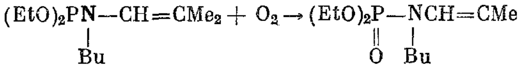
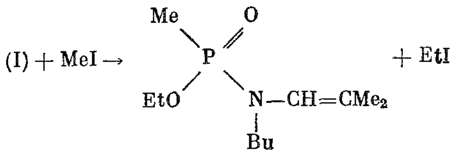
We have recently synthesized amidophosphites containing a vinyl group at the nitrogen atom [1, 2] and studied the reactions of these compounds with α-chloracetaldehydes [2]. In a further study of these compounds, we have discovered that diethyl N-butyl-N-isobutenylamidophosphites (I) reacts readily with atmospheric oxygen. An exothermic reaction with heating up to 120°C occurs upon bubbling oxygen through phosphite (I) to form diethyl N-butyl-N-isobutenylamidophosphate (II). The reaction of (I) with sulfur proceeds analogously



$$(EtO)_2P\underset{Bu}{N}{-}CH{=}CMe_2 + O_2 \rightarrow (EtO)_2\underset{O}{P}{-}\underset{Bu}{N}CH{=}CMe_2$$

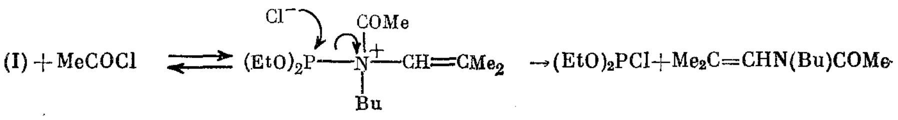
(I) (II)

Phosphite (I) reacts with MeI by the Arbuzov rearrangement to form ethyl N-butyl-N-isobutenylamidomethylphosphonate (III) and EtI



(III)

It is interesting that (I) reacts with acetyl chloride similarly to aliphatic amides of dialkylphosphorous acids [3] to form diethylchlorophosphite and N-butyl-N-isobutenylacetamide (IV). The most likely pathway for these reactions involves initial nucleophilic reaction of the amidophosphite nitrogen atom with the carbonyl carbon of the acyl halide [4, 5].



(IV)

Trialkyl phosphites and ester-amides of phosphorous acid undergo a complex reaction with CCl_4. An increase in the number of amide groups at the phosphorus atom in going from tri-

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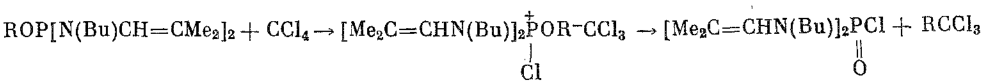
alkyl phosphites to esters of mono- and diamidophosphorous acids leads to a change in the course of the reaction. Trialkyl phosphites react with CCl_4 to form exclusively dialkyltrichloromethylphosphonates [6], while amides of dialkylphosphorous acids react with CCl_4 to form alkyl-N,N-dialkylamidotrichloromethylphosphonates and the corresponding chlorophosphates [7]. Diamidophosphites react with CCl_4 to form only chlorophosphates [8]. In a continuation of these studies, we investigated the reaction of CCl_4 with esters of bis(N-butyl-N-isobutenylamido) phosphorous acid. The reaction of ethyl bis(N-butyl-N-isobutenylamido) phosphite (V) with CCl_4 gives bis(N-butyl-N-isobutenylamido)chlorophosphate (VI) and 1,1,1-trichloropropane. The reaction of trimethylsilylbis(n-butyl-N-isobutenylamido)phosphite proceeds analogously:



$$\mathrm{ROP[N(Bu)CH{=}CMe_2]_2 + CCl_4 \rightarrow [Me_2C{=}CHN(Bu)]_2\underset{\underset{Cl}{|}}{\overset{+}{P}}OR^{-}CCl_3 \rightarrow [Me_2C{=}CHN(Bu)]_2\underset{\underset{O}{\|}}{P}Cl + RCCl_3}$$

(VI)

R = Et, $SiMe_3$

The trichloromethyl anion in the reactions of dialyl trimethylsilylphosphites with CCl_4 also desilylates the intermediate to form a chlorophosphate and trimethyltrichloromethylsilane [9].

EXPERIMENTAL

Diethyl N-Butyl-N-isobutenylamidophosphate (II). Dry oxygen was bubbled through 11.9 g (I). The mixture heated to 120°C and was maintained for 3 h at about 20°C. Distillation in vacuum gave 8.8 g (69.5%) (II), bp 78-80°C (0.1 mm), d_4^{20} 0.9893, n_D^{20} 1.4438. Found, %: C 54.92; H 9.95; N 5.26; P 11.69. $C_{12}H_{26}NO_3P$. Calculated, %: C 54.75; H 9.89; N 5.32; P 11.79. δ ^{31}P 6 ppm, ν(P=O) 1270, ν(C=C–N) 1680 cm^{-1}.

Ethyl N-Butyl-N-isobutenylamidomethylphosphonate (III). A sample of 6.4 g MeI was added with water cooling to 11.2 g (I) and the mixture was maintained at about 20°C prior to vacuum distillation which yielded 9.2 g (87.1%) (III), bp 116-118°C (0.8 mm), d_4^{20} 0.9686, n_D^{20} 1.4542. Found, %: C 56.66; H 10.72; N 6.09; P 13.07. $C_{11}H_{24}NO_2P$. Calculated, %: C 56.65; H 10.30; N 6.01; P 13.30. δ ^{31}P 30 ppm, ν(P=O) 1270, ν(C=C–N) 1675 cm^{-1}. EtI was collected in a liquid nitrogen trap, 6.4 g (90.5%), bp 72°C, d_4^{20} 1.9308, n_D^{20} 1.5112.

N-Butyl-N-isobutenylacetamide (IV). A sample of 4.8 g acetyl chloride was added to 15.2 g (I) at –40°C and the mixture was gradually warmed to 20°C, maintained for 3 h, and distilled in vacuum to yield 7.4 g (77.1%) diethyl chlorophosphite, bp 63-65°C (30 mm), d_4^{20} 1.0767, n_D^{20} 1.4356 [10], δ ^{31}P 165 ppm. 8.1 g (77.9%) (IV), bp 100-102°C (10 mm), d_4^{20} 0.8992, n_D^{20} 1.4568. Found, %: C 71.23; H 11.16; N 8.38. $C_{10}H_{10}NO$. Calculated, %: C 71.01, H 11.24 N 8.28. ν(C=N)1675, ν(C=O) 1650 cm^{-1}.

Trimethylsilylbis(N-butyl-N-isobutenylamido)phosphite (VIII). A sample of 127 g bis(N-butyl-N-isobutenylamido)chlorophosphite was added dropwise to a mixture of 7.2 g water, 80.6 g Et_3N, and 500 ml pentane at 4°C. The mixture was maintained for 15 min and then warmed to 15°C. Then, 43.2 g Me_3SiCl was added dropwise. The mixture was left standing overnight and the precipitate was filtered off. The solution was distilled off and the residue was distilled in vacuum to yield 75 g (50.4%) (VII), bp 107-110°C (0.4 mm), d_4^{20} 0.8921, n_D^{20} 1.4680. Found, %: C 61.25; H 11.09; N 8.05; P 8.06; Si 7.29. $C_{19}H_{41}N_2OPSi$. Calculated, %: C 61.29; H 11.02; N 7.53; P 8.33; Si 7.53. δ ^{31}P 120 ppm, ν(C=C–N) 1675 cm^{-1}.

Reaction of Ethyl Bis(N-butyl-N-isobutenylamido)phosphite (V) with CCl_4. A sample of 5.1 g CCl_4 was added dropwise to 8.1 g (V) at –30°C and the mixture was maintained at ~20°C for 3 h. Vacuum distillation gave 4.4 g (53.1%) (VI), bp 141-144°C (0.6 mm), d_4^{20} 1.0092, n_D^{20} 1.4832. Found, %: C 57.00; H 9.76; N 8.58; P 9.01; Cl 11.05. $C_{12}H_{32}N_2OPCl$. Calculated, %: C 57.40; H 9.57; N 8.37; P 9.27; Cl 10.61. A yield of 4.1 g (83.8%) 1,1,1-trichloropropane was collected in a liquid nitrogen trap, bp 102°C, d_4^{20} 1.2880, n_D^{20} 1.4550 [7].

Bis(N-butyl-N-isobutenylamido)chlorophosphate (VIII). A sample of 2.6 g CCl_4 was added dropwise to 6.2 g (VII) at –30°C. The mixture was maintained for 3 h at ~20°C and then distilled in vacuum to yield 3 g (53.8%) (VIII), bp 138-140°C (0.04 mm), d_4^{20} 1.0097, n_D^{20} 1.4850. δ ^{31}P 20 ppm, ν(P=O) 1200-1300, ν(C=C–N) 1675 cm^{-1}. A yield of 2.1 g (65.8%) trimethyltrichloromethylsilane was collected in a liquid nitrogen trap, mp 43°C (from pentane) [9], δ ^{1}H 0.35 ppm.

CONCLUSIONS

1. Dialkyl N-butyl-N-isobútenylamidophosphites are readily oxidized by oxygen, react with methyl iodide to form the corresponding methyl phosphonates, and react with acetyl chloride to give a dialkyl chlorophosphite and N-butyl-N-isobutenylacetamide.

2. Ethyl and triethylsilyl bis(N-butyl-N-isobutenylamido)phosphites react with carbon tetrachloride to form bis(N-butyl-N-isobutenylamido)chlorophosphate and 1,1,1-trichloropropane and trimethyltrichloromethylsilane, respectively.

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SPECIAL FEATURES OF THE SOLUBILITY OF ARGON IN SOLVENTS WITH A THREE-DIMENSIONAL HYDROGEN BOND FRAMEWORK

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The gas solubility method is widely used for studying the structural features of pure and, especially, mixed solvents [1]. This method permits the detection of changes which occur in solvents but are not revealed by other methods. The solubility of gases in aqueous solutions of nonelectrolytes has been studied extensively, but fewer investigations have been carried out on gas solubility in the aqueous solutions of electrolytes [2]. Only a few studies have been devoted to nonaqueous mixed electrolytes. It is generally assumed that the addition of an electrolyte to water leads to a decrease in gas solubility (Sechenov rule). However, our studies of the solubility of argon in aqueous solutions of tetraalkylammonium halides [3] and in aqueous solutions of chloropentaamminecobalt(III) chloride [4] showed that the solubility of argon passes through a maximum with increasing concentration of the salt in the region of low electrolyte concentrations at low temperatures. This effect was previously reported only for the aqueous solutions of several nonelectrolytes [5]. Hence, we attempted to determine whether this nature for the dependence of the argon solubility on the salt concentration is unique for aqueous solutions. For this purpose, we studied the solubility of argon in nonaqueous solutions of tetraethylammonium chloride in ethyleneglycol.

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